

PB-241 802

INVESTIGATION OF THE ORION RESEARCH CYANIDE
MONITOR

Robert J. O'Herron

National Environmental Research Center
Cincinnati, Ohio

April 1975

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE

TECHNICAL REPORT DATA (Please read Instructions on the reverse before completion)		
1. REPORT NO. EPA-670/4-75-005	2.	3. PB 241 802
4. TITLE AND SUBTITLE INVESTIGATION OF THE ORION RESEARCH CYANIDE MONITOR		5. REPORT DATE April 1975; Issuing Date
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Robert J. O'Herron		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS National Environmental Research Center Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268		10. PROGRAM ELEMENT NO. 1HA327; ROAP 01AAD, TASK 02C
		11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Same as above.		13. TYPE OF REPORT AND PERIOD COVERED
		14. SPONSORING AGENCY CODE
15. SUPPLEMENTARY NOTES		
16. ABSTRACT The model 1206 Orion Research cyanide monitor was investigated using the Orion specifications and environmental considerations as a guide. Laboratory tests under controlled environmental conditions showed the electronic stability (drift) to be within 0.1% over the temperature range of 5C to 35C. Sensor stability, over the temperature range 5C to 35C was tested by applying free cyanide ion (standard solutions of 1 mg/l and 10 mg/l) as direct input to the monitors. The results of these tests showed that Orion's specified tolerance of $\pm 10\%$ of reading was met. Two out of three electrode sets tested for linearity were within Orion's tolerance of ± 0.02 ppm below 0.25 ppm and $\pm 10\%$ of readings above 0.25 ppm Dynamic on-stream measurements were made from a metal plating process rinse stream in a field installation of the monitor, and these measurements were periodically compared with those of the standard method for total cyanide. This field installation revealed the comparisons were widely variable. Steady-state comparisons were made of field-collected samples with the standard method for determining total cyanide. These tests revealed that a 15% to 20% loss in cyanide concentration resulted from the required straining and filtering of the sample input to the monitor.		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS Activity coefficients, *Cyanides, *Monitors, *Metal complexes, *Performance evaluation. Reproduced by NATIONAL TECHNICAL INFORMATION SERVICE U.S. Department of Commerce Springfield, VA. 22151	b. IDENTIFIERS/OPEN ENDED TERMS Activity, Free ions, Ionic interferences, Ionic strength, *Ion-selective electrode, Reagent additions, *Specific ion electrodes, Total concentration, *Total cyanide.	c. COSATI Field/Group 13B
18. DISTRIBUTION STATEMENT Release to public	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 32
	20. SECURITY CLASS (This page) Unclassified	22. PRICE 3.75/2.25

EPA-670/4-75-005
April 1975

INVESTIGATION OF THE ORION RESEARCH CYANIDE MONITOR

By

Robert J. O'Herron

Methods Development and Quality Assurance Research Laboratory

Program Element No. 1HA327

NATIONAL ENVIRONMENTAL RESEARCH CENTER
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

ia

REVIEW NOTICE

The National Environmental Research Center--Cincinnati
has reviewed this report and approved its publication.
Mention of trade names or commercial products does not
constitute endorsement or recommendation for use.

FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multi-disciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

This report is part of a continued effort by the Instrumentation Development Branch, Methods Development and Quality Assurance Research Laboratory (MDQARL), NERC-Cincinnati, to investigate instruments and provide information to both users and suppliers. The intention is also to upgrade instrumentation, and to make it possible to choose the most suitable instrument for a particular application.

A. W. Breidenbach, Ph.D.
Director
National Environmental
Research Center, Cincinnati

ABSTRACT

The model 1206 Orion Research cyanide monitor was investigated using the Orion specifications and environmental considerations as a guide. This is one of the Series 1000 monitors manufactured by Orion which duplicate laboratory analyses made with ion-selective electrodes. The Series 1000 monitors perform single parameter measurements of concentration, it is reported, and continuously display the results on a panel meter and a strip chart recorder. Sample pretreatment techniques are applied against an array of interferences encountered in the use of ion-selective electrodes. The cyanide monitor employs a silver/sulfide--sodium reference electrode set in the indicator method to detect, continuously, the level of cyanide in a sampled stream. Cadmium, copper, nickel, and zinc complexes of cyanide are broken by two reagents added in the fluids-chemical section. The breakdown of tightly bound cyanide complexes of iron, cobalt, and platinum are not effected by the addition of these reagents. Hydrogen cyanide (HCN) is converted to the free cyanide ion for detection by the electrodes.

Laboratory tests under controlled environmental conditions showed the electronic stability (drift) to be within 0.1% over the temperature range of 5C to 35C. Sensor stability, over the temperature range 5C to 35C was tested by applying free cyanide ion (standard solutions of 1 mg/l and 10 mg/l) as direct input to the monitors. The results of these tests showed that Orion's specified tolerance of $\pm 10\%$ of reading was met. Two out of three electrode sets tested for linearity were within Orion's tolerance of ± 0.02 ppm below 0.25 ppm and $\pm 10\%$ of readings above 0.25 ppm cyanide concentration.

Dynamic on-stream measurements were made from a metal plating process rinse stream in a field installation of the monitor, and these measurements were periodically compared with those of the standard method for total cyanide. This field installation revealed the comparisons were widely variable. Steady-state comparisons were made of field-collected samples with the standard method for determining total cyanide. These tests revealed that a 15% to 20% loss in cyanide concentration resulted from the required straining and filtering of the sample input to the monitor.

CONTENTS

	<u>Page</u>
Abstract	iv
List of Figures and Tables	v
Acknowledgments	vi
Sections	
I Conclusions	1
II Recommendations	4
III Introduction	5
IV The Orion Cyanide Monitor	8
V Laboratory Evaluation	11
VI Field Evaluation	17
VII Laboratory Tests with Field Sample	22
VIII References	24

FIGURES AND TABLES

Figure Number		
1	Series 1000 Monitors	8
2	Block Diagram of the Chemical Sensing Section	10
3	Preamplifier Output Voltage--CTA Temperature Transition from 45C to 30C	14
4	Fluid Connections to Monitor	17
5	Regression Line with 95% Confidence Limits for the Mean Response	21
Table Number		
1	Ten Day Operation	11
2	Environmental Tests with Continuous Measurement of Sample	13
3	Linearity and Lower Limit Detection of Cyanide Standards	15
4	Comparison of Cyanide Monitor Field Installation Data with Laboratory Analysis of Total Cyanide	20
5	Relative System Response with Varying Pressure Input	22
6	Laboratory Test with Cyanide Waste Samples Col- lected in the Field	23

ACKNOWLEDGMENTS

We gratefully acknowledge the support and help of L. B. Lobring (Physical and Chemical Methods Branch, MDQARL) in preparing standards and analyzing samples; P. P. Kovatis (of the Metal Finishers Foundation) in securing industry cooperation to permit the monitor to be installed on a cyanide waste stream; R. P. Lauch (Instrumentation Development Branch, MDQARL) for contributing suggestions that helped in selecting hydraulic test apparatus; and T. J. Stasiak and W. T. O'Connell (Orion representatives) for their installation assistance and helpful suggestions throughout this investigation.

SECTION I

CONCLUSIONS

1. Modification in components and procedures made by Orion during the interval of this evaluation of the cyanide monitor indicated the model tested was still in the prototype stage of development.
2. Being in an early stage of production, some improvements in quality control of components appear to be necessary.
3. Electronic drift at constant temperature (20C) was less than 0.1% for a 1-week interval.
4. Electronic drift over the temperature range 5C to 35C was 0.12%.
5. Sensor drift over the temperature range 5C to 35C was within Orion's specified tolerance of $\pm 10\%$ of reading for cyanide standards of 1 mg/l and 10 mg/l. This occurs if the operation is within Orion's framework: the constant temperature assembly is maintained 5C above ambient temperatures of 25C and the automatic restandardization has taken place after the temperature change.
6. Two of three electrode sets tested were within Orion's tolerance of ± 0.02 ppm on concentrations below 0.25 ppm cyanide and $\pm 10\%$ of reading on concentrations above 0.25 ppm cyanide. The other electrode set ranged slightly higher--to within 0.04 ppm on concentrations below 0.25 ppm cyanide.
7. As a result of this investigation, Orion has had the instruction manual, which lacked clarity and depth, rewritten and broadened in scope.
8. Data from the cyanide monitor installed in a field location varied widely from the standard method determinations of total cyanide. This variability was caused by:
 - a. an inability to maintain input pressure to the filter at the recommended 15 to 20 psi: the strainer and a throttling valve clogged when the monitor was unattended,

- b. a drop in cyanide concentration across the strainer and filter,
 - c. an inability of the monitor to measure total cyanide, and
 - d. the long delay (8 to 10 minutes with adequate pressure input) of fluids in transit and of electrode response dampened the abrupt and cyclic variations in cyanide concentrations of the wastewater sampled. (Note: Discussions with Orion personnel about problems encountered in maintaining suitable pressure input to the filter has resulted in a new prefilter design.)
9. Steady-state tests with field samples showed that a 15% to 20% loss in cyanide concentration occurred across the strainer and filter.
 10. Essentially all of the cyanide passing the filter was measured by the monitor for these particular samples. (Note: This is sample dependent.)
 11. Response time to a change in cyanide concentration was a function of the sample input pressure.
 12. As a result of the number of tests and the length of time necessary to complete these tests, there were no long-term tests made of the effectiveness of either the electrodes (4 month replacement) or the filter (1 month replacement).
 13. The monitor does not measure iron, cobalt, platinum, gold, and silver complexes of cyanide. Chlorine is a negative interference. High levels of sulfide (10 mg/l and above) cause a positive interference and must be avoided. Orion continues its research effort to counteract these interferences.
 14. In summary, the cyanide monitor includes stable electronics that performed very well over changing environmental conditions. Ambient temperature should be controlled, not to exceed 30C because high temperature reduces the life of the electrodes. Fluids flow requires that the temperature be controlled above 0C. The reference voltage feedback technique employed in the automatic restandardization approach is clever; it is effective in compensating for the long-term drift that's encountered in the use of ion-selective electrodes. Application of the monitor should not be considered

routine. Care and maintenance will be a continuing requirement. Qualified personnel, aware of sample characteristics and monitor limitations, are required to interpret the data; i.e., qualified chemists should perform periodic comparison tests with the standard method for total cyanide. The monitor measures some of the loosely bound metal cyanide complexes, but not those which are tightly bound. The presence and the effect of other interferences, e.g., chlorine and sulfide, on the electrode signal output should be known.

SECTION II

RECOMMENDATIONS

The Orion cyanide monitor does not measure total cyanide, and problems were encountered with its use. However, the standard method for measuring total cyanide cannot be performed rapidly, unattended, inexpensively, continuously, or with few problems. Each method performs capably in some category. Therefore, it is recommended that the desirable qualities of each be utilized to their fullest extent. The cyanide monitor cannot measure total cyanide, but with care and proper maintenance, it can measure some forms of the cyanide present in certain wastes. And Orion is planning future improvements. At present, the cyanide monitor can be used where continuous surveillance is required on wastes suspected of having excessive cyanide. Dual set-point, high- and low-alarm limits, included in the monitor, can be employed to actuate a sampling device when a predetermined limit has been exceeded. Thus, samples can be screened in the field so that the time-consuming analysis of the standard method for total cyanide can be expedited. If it can be shown that positive interferences are not present, gross violations of effluent standards as indicated by a calibrated and functional monitor, should be useful.

The Orion Series 1000 monitors are designed and developed to meet needs of Industry. As a result of these developments, as in the case of the cyanide monitor, these instruments could also be of use to EPA procurements provided the application and performance requirements are well defined.

SECTION III

INTRODUCTION

Ion-selective electrodes developed within the past two decades have been employed with instrument systems under favorable process conditions for control purposes. Generally, these instruments were utilized as indicators of gross process upsets. The mere presence of a measured parameter could be indicative of a breakdown at some point within a process. In these earlier process control applications of ion-selective electrodes, pretreatment of the sample has primarily involved obtaining favorable pH and controlling the temperature. These instrument systems measured sample parameters under favorable process conditions and performed useful control functions in industrial processes. That is, the uncomplexed, free ion was measured in samples where interferences were known to be minimal.

In recent years, several manufacturers have made a concerted effort to use continuous monitors for concentration values of parameters. Interferences encountered with the use of ion-selective electrodes make it necessary to pretreat the sample in monitoring systems. The interferences can be due to the sample itself or to the measuring electrode and the reference electrode. Ion-selective electrodes respond to the free, unbound ion, not the total concentration of a chemical species. Increased use of ion-selective electrodes in laboratory analyses over the years has resulted in methods being developed to free bound ions so that concentrations can be determined. Ions resulting in electrode interferences must be either removed or avoided through chemical pretreatment techniques. The amount and type of other ions in solution (ionic strength)¹ affect the signal output of ion-selective electrodes. The activity, a , of an ion is related to the concentration, C , by the equation

$$a = \gamma C \quad (1)$$

where γ is the activity coefficient, which is dependent upon the total ionic strength of the solution. Ionic strength adjusters (ISA) are available that when added to standardizing solutions and samples, "swamp out" differences so that the activity coefficient of the ion being sensed is about the same in all solutions.

The pH of the sample may also result in interferences: bound ions

may be decomplexed at a favorable pH or interfering ions may be preferentially complexed within a certain pH range. In addition, either the hydrogen (H^+) or hydroxyl (OH^-) ions may be an electrode interference. Therefore, sample pH adjustment is a usual requirement.

The voltage output of ion-selective electrodes is characterized by the Nernst equation at constant temperature.

$$E = E^\circ + (0.19841T/n) \log a_i \quad (2)$$

The variation as a result of temperature change is described by T. S. Light.²

$$\begin{aligned} dE/dT = dE^\circ/dT + (0.19841/n) \log a_i + \\ (0.19841T/n)(d \log a_i/dT) \end{aligned} \quad (3)$$

Sample temperature affects not only the Nernstian slope term $[(0.19841/n) \log a_i]$, but also the "solution temperature coefficient" term $[0.19841T/n)(d \log a_i/dT)]$. Light has discussed the solution temperature coefficient term:

"The activity of an ion may be affected by its activity coefficient and for weak or complex forming electrolytes by its equilibrium relationships. Since activity coefficients and equilibrium constants may each have temperature coefficients of their own, the 'solution temperature coefficient' term may become quite complex."

Because temperature compensation techniques normally correct for the Nernst slope term only, temperature control of the sample is generally selected by Orion. Sample color and turbidity do not interfere with the voltage relationships in the use of ion-selective electrodes. Filtering is necessary, however, to combat clogging of tubing or fouling of electrodes.

In regard to reference electrodes, Orion has stated, "Our experience over the past several years has shown that most of the problems that users of specific ion electrodes have reported to us are directly traceable to the liquid junction in the external reference electrode."³ Requirements for 0.1 to 0.2 mv accuracy

for 1% to 2% ion activity, as opposed to approximately 6 mv to obtain 0.1 pH unit accuracy, were indicated. These tougher requirements for specific ions have led Orion to advise using a second specific ion electrode,⁴ as a reference electrode--one whose level can be kept constant.

SECTION IV

THE ORION CYANIDE MONITOR

The cyanide monitor, reported on here, is one of the Series 1000 monitors⁵ manufactured by Orion Research (Figure 1). These are single-parameter, continuous analyzers designed to duplicate laboratory measurements made with ion-selective electrodes in an industrial environment. A bypass filtration system feeds a sample stream to a constant-temperature assembly (CTA), which is thermostated to maintain both the sample and electrodes at the same temperature. A daily, automatic operation check is made with a calibrating standard solution, and if an error is encountered, it is automatically corrected. In most cases, reference potentials are established by using ion-selective electrodes to detect high and constant levels of ions inserted in reagents. Orion has indicated that monitoring systems can be designed for all laboratory methods of analysis utilizing ion-selective electrodes.

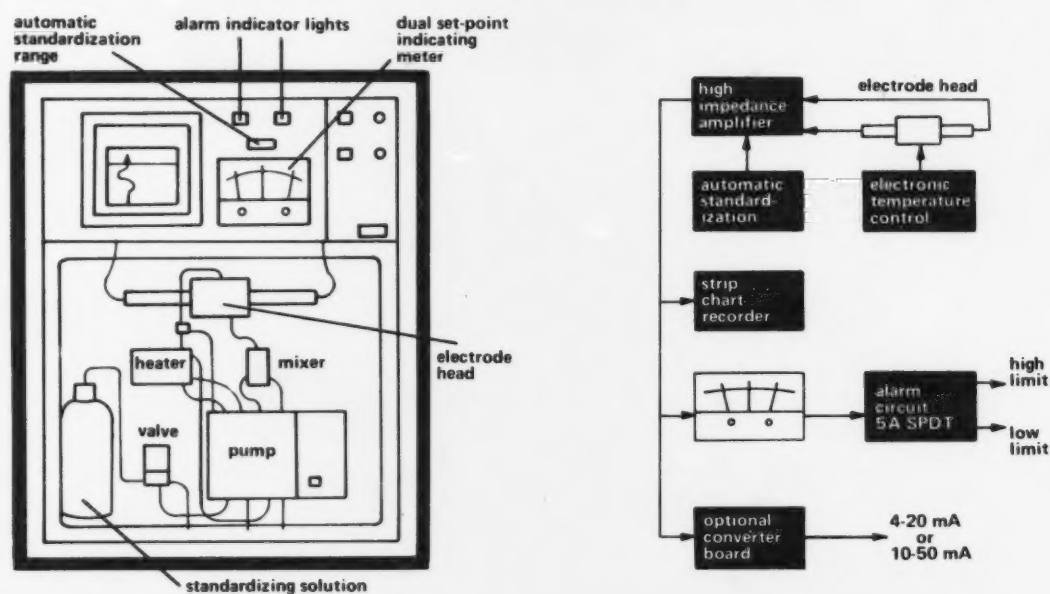
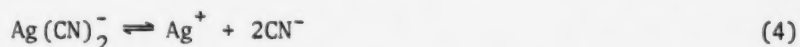


Figure 1. Series 1000 monitors (courtesy of Orion Research Incorporated).

The cyanide monitor employs a silver/sulfide and sodium reference electrode set in the indicator method⁶ to detect the level of cyanide in a sampled stream. Two reagents are added as pretreatment to remove cyanide from metal complexes, such as nickel and copper, that are not complexed by OH⁻ ion. Heating at a temperature of 80C in the reaction heater speeds the breakdown of metal cyanides and the formation of hydrogen cyanide (HCN) gas. Other metals, such as zinc and cadmium, preferentially complex with OH⁻ ion rather than cyanide. Therefore, sodium hydroxide (NaOH) is added; to complex these metals, allow the formation of metal EDTA complexes, and convert the HCN gas to the free cyanide ion. A sodium ion-selective electrode detects the high, constant sodium ion level added and it establishes the reference potential. The base reagent also contains the indicator in the form of a silver cyanide complex (KAg(CN)₂). The following equilibrium is established:



The excess cyanide in the sample shifts this reaction to the left and results in a lowering in the free silver ion. The silver/sulfide electrode detects the lower silver activity, and responds with a more negative electrode potential. The silver/sulfide electrode effectively, then, responds to the cyanide ion. However, since two cyanide ions are present for each silver ion, the theoretical Nernst slope is -118 mv per decade, or twice the normal for a univalent ion. The silver/sulfide electrode indicator method for determining cyanide is sensitive to lower levels of cyanide than is the cyanide ion-selective electrode. Also, greater precision in measurements are enabled with the -118 mv slope. A block diagram of the fluids-chemical sensing section of the cyanide monitor is shown in Figure 2.

It should be emphasized that the silver/sulfide electrode responds to free cyanide ion. The reagents added free the cyanide from several metal complexes. Other cyanide metal complexes, such as iron, cobalt, and platinum, are resistive to decomposition and are not measured by the monitor. Excessive amounts of sulfide can also be an interference.

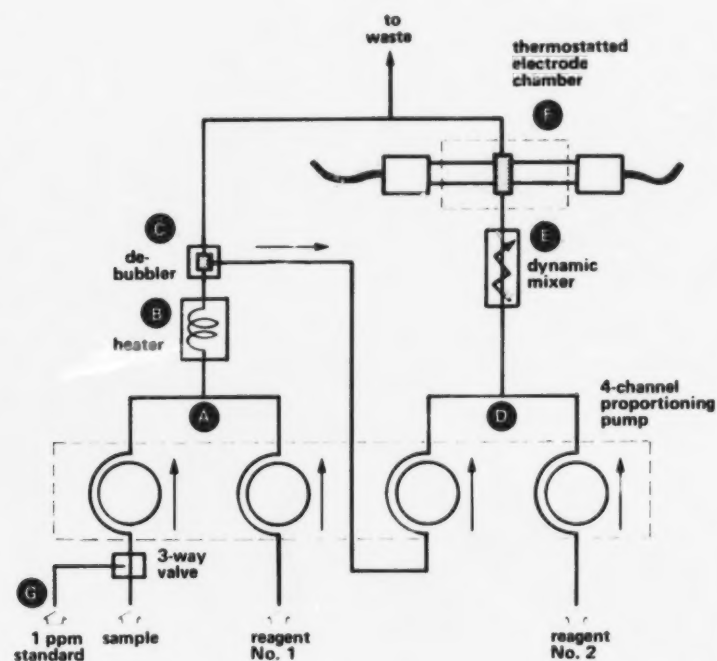


Figure 2. Block diagram of the chemical sensing section (courtesy of Orion Research Incorporated).

The original purchase price of the cyanide monitor was \$5300. With continuous operation, there is the continuing reagent and supply costs. A contract that provided replacements for reagents and for all expendable monitor supplies on a yearly basis was \$1750. The replacement schedule is based on 1 year of continuous, 24-hour-per-day operation. For those who wish to operate intermittently, unit costs for supplies are approximately 35% greater.

The cyanide monitor requires 115V ($\pm 10\%$), 60 Hz, single-phase power at 100 watts. The system is housed in a NEMA 12 case, 86 cm high by 69 cm wide by 36 cm deep (33 in. by 27 in. by 14 in.), and has a mass of 68 kg (200 lb). The two reagents are supplied in 3.785-liter (5 gal) containers.

SECTION V

LABORATORY EVALUATION

Laboratory testing consisted of applying standard solutions, without filtering, as direct input to the monitor. Initially, these solutions consisted of free cyanide ion in 1.0 M potassium hydroxide (KOH). These tests included continuous monitoring of a 0.1 mg/l cyanide standard over a 10-day interval, environmental testing from 5C to 35C, and linearity tests over a three-decade span of from 0.01 mg/l to 10 mg/l cyanide. Problems encountered during this interval are discussed at the end of this section.

The 2.2 ml/min sample input needs of the monitor required that 34 liters (nearly 10 gal) of 0.1 mg/l cyanide standard be made up for the 10-day test. A 1 mg/l cyanide restandardization solution was automatically applied each day, and electrode drift was corrected automatically. Tests were made colorimetrically on the sample and compared with the monitor readings. Table 1 illustrates the results.

Table 1. TEN-DAY OPERATION TEST

Day	Monitor		Colorimeter, mg/l	Restandardization meter, μ amperes
	Recorder, mg/l	Panel meter, mg/l		
	0.048	0.048	--	-1
4	0.110	0.110	--	+2
	0.095	0.095	0.099	+2
5	0.100	0.100	--	0
	0.090	0.090	0.095	0
6	0.100	0.100	--	0
	0.097	0.097	--	0
7	0.088	0.086	--	0
	0.085	0.084	0.099	0
8	0.085	0.085	--	0
	0.084	0.081	0.100	0
10	0.074	0.071	--	0
	0.086	0.084	0.097	+4
	0.084	0.084	--	+4

All of the colorimetric determinations would have been reported as 0.1 mg/l cyanide; this indicates that the sample remained stable over the 10-day interval. The initial monitor reading was low. Thereafter, the value rose through a transitory interval (not described because of recorder ink flow stoppage) to a more correct value. The ensuing monitor reading remained within Orion's specified ± 0.02 mg/l tolerance of the 0.1 mg/l standard for all except 1 day. The restandardization cycle on that one evening returned the recorded values to within tolerance.

Attempts were made to apply a d.c. millivolt source as input to the monitor so that electronic stability tests could be made. These attempts were unsuccessful because the circuit and potentials generated by the electrodes in samples could not be duplicated accurately. Orion's suggestion of utilizing shorting straps across the input and adjusting for midscale readings (zero voltage output from the preamplifier) was followed. A ± 50 mv (zero midscale) recorder was placed on the preamplifier output (input to the Leeds and Northrup (L&N) recorder utilized by Orion). A 0- to 5-V recorder was placed on the output of the Voltage/Current Converter. Zero input to the converter resulted in a midscale output of 2.5 V d.c. The cyanide monitor was installed in an environmental chamber and operated at 20C for a 1-week interval to observe drift under these conditions. The results of this test indicated no apparent drift from the converter output tracing, but the drift on the more sensitive ± 50 mv recorder on the preamplifier ranged between 0 and 1.3 mv. That is, a drift of less than 0.10% of the full-scale output range.

With the constant-temperature drift established, the ambient temperature within the chamber was reduced in steps to 5C, returned to 20C, and increased in steps to 35C. Thermocouples were placed in the reaction heater, CTA, electronics enclosure, and enclosed cyanide monitor cabinet space and at points within the environmental chamber exterior to the monitor. The minimum adjustable setting for the CTA was 30C. The preamplifier output drift ranged between ± 3 mv or 0.12% of the output span. Again, this small variation was of little consequence with the resolution of the 0 to 5 V d.c. output recorders. The minimum adjustable temperature setting of the CTA had no adverse affect at the lower ambient temperatures. For temperatures above 25C, the CTA was adjusted within Orion's framework of 5C above ambient. The 80C temperature of the reaction heater was beyond the 65C maximum of the thermocouple recorder used. However, with reduction of the ambient

temperature to 2C, one of the thermocouples within the reaction heater began to indicate just below the 65C, full-scale reading of the thermocouple recorder. The effect of this upon cyanide metal complex destruction with reagent addition in the reaction heater was not pursued.

Further environmental tests over the 5C to 35C temperature range were conducted with the electrodes included to continuously monitor cyanide standards. Automatic restandardization was performed daily, and the CTA temperature was maintained at 5C above 25C ambient temperatures as before. The base background of the standards was changed to 0.01 M NaOH for 1 mg/l cyanide standards and 0.005 M NaOH for 10 mg/l cyanide standards. Two-liter volume standards were made for calibration and restandardization purposes, and 17 liters (nearly 5 gal) of standards were made for continuous monitoring. The intent of the test was to observe whether, for values over 0.25 ppm cyanide, the continuous reading remained within the specified $\pm 10\%$ of reading over the specified temperature range. Manual calibrations were performed at 20C before both the decrease and the increase in ambient temperature. The large-volume samples were replenished at this time, also. After stabilizing, restandardization, and adjusting the CTA temperature, at each temperature if necessary, the input was changed between the 1 mg/l cyanide and 10 mg/l cyanide samples. After a sufficient time lapse to allow for both sample transit through the system and electrode response time, readings were taken from the L&N strip chart recorder (Table 2).

Table 2. ENVIRONMENTAL TESTS WITH CONTINUOUS MEASUREMENT OF SAMPLE

Temperature C	Cyanide sample, mg/l		Cyanide standards, mg/l		Remarks
20	1.00	12.0	1.0	10.0	calibrated
10	0.99	12.1	1.0	--	
5	0.95	12.8	0.9	--	
20	1.05	10.1	1.0	10.0	calibrated, and replen- ished sample
30	1.90	10.2	1.0	10.0	
35	1.10	10.8	1.1	10.5	observed noise

Table 2 illustrates that all of the data are within $\pm 10\%$ of the original calibration values at 20C. For example, after calibration with the standard, the signal output for the sample ranged from the original value of 12 mg/l at 20C to 12.8 mg/l at 5C. The sample was then replenished, a calibration was made, and the signal output ranged from 10.1 mg/l at 20C to 10.8 mg/l at 35C. Figure 3 illustrates the transistion of the preamplifier output from 35C at the left to 20C at the right, which was the conclusion of the test. The corresponding CTA temperatures were above 40C to 30C. The large noise component is clearly indicated. The actual output noise, although present, is very much less than is indicated here. Figure 3 merely expands 0.1 V about zero voltage of the ± 2.5 V output of the preamplifier. Orion has indicated that the electrode lifetimes were shortened by operation at higher temperature, it would be advisable to provide cooling where 30C ambient temperatures are exceeded.

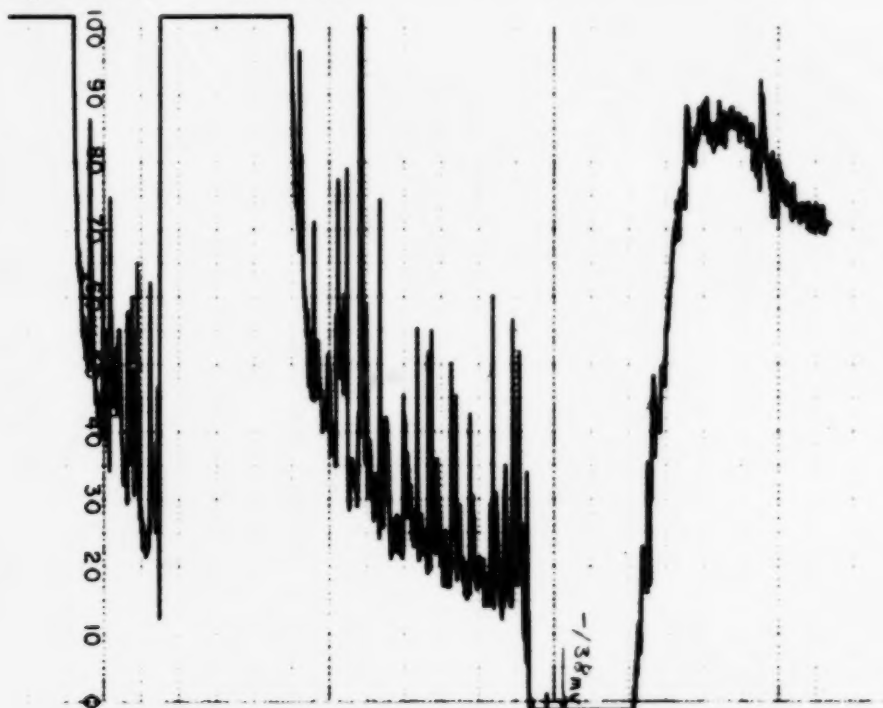


Figure 3. Preamplifier output voltage; CTA temperature transistion from 45C to 30C.

Linearity and lower-limit detection tests were performed on cyanide standards with three separate cyanide electrode sets. The accuracy specifications listed by Orion for the cyanide monitor is ± 0.02 ppm up to 0.25 ppm and $\pm 10\%$ of reading above 0.25 ppm. The specified lower limit of detection is 0.05 ppm cyanide. The three electrode sets were installed in the monitor and precalibrated with 1 mg/l and 10 mg/l cyanide standards. Standards ranging from 10 mg/l to 0.01 mg/l were applied as input to the monitor; the results are illustrated in Table 3.

Table 3. LINEARITY AND LOWER LIMIT DETECTION
OF CYANIDE STANDARDS

Electrode set	Cyanide standards, mg/l					
	10.0	1.0	0.10	0.05	0.03	0.01
B	10.0	0.98	0.11	0.060	0.042	0.023
C	10.0	1.00	0.14	0.082	0.058	0.034
D	10.0	1.00	0.12	0.076	0.052	0.031

Electrode set B performed within the Orion specifications for all the standards listed. Electrode set C ranged between 0.024 mg/l and 0.04 mg/l high for all values below 0.25 mg/l. Electrode set D indicated nearly correct for all values, but the response times were approximately 15 minutes longer than those for the other two electrodes because of excessive drift.

Problems encountered in the laboratory testing of the cyanide monitor extended the evaluation period beyond the previously allotted time interval. These problems are related to help future users and to inform Orion of areas in which the instrument and quality control procedures might be improved. Some improvements were made during the evaluation period, and, in a sense, the monitor is still a prototype that can be updated and improved. To date, however, the systems engineering and the merging of the disciplines of hydraulics, mechanics, electronics, and chemistry in this instrument are commendable.

To summarize, problems were encountered in the output display section, the fluid-chemical sensing section, electronics assembly, sensor electrodes, and in standards preparation. The recorder required service by L&N twice as a result of inking problems and erroneous tracking. The severe inking problems were corrected,

but occasional ink flow disruptions occurred throughout the evaluation. The inking was particularly unreliable at ambient temperatures of 35C and 40C. The tracking problems were corrected when the balancing motor brushes were cleaned. Chart take-up failures occurred when the reroll-drive spring separated and again when the chart take-up neared the end of a roll of chart paper.

Leaks occurred at two points within the fluids-chemical sensing section, i.e., the reaction heater and the 3-way waste junction connector. The 24-volt power supply failure was the only disruption resulting from electronic failure. The original electrode set failed, according to Orion, because of repeated temperature shocks experienced during transistions between idle and operating intervals. Orion indicated that a lower quality sodium glass temporarily employed in the reference electrode was the primary cause of the sensor drift. The suitability of the electrodes received thereafter confirms this. The change in the standards concentration from a difficult molarity concentration to 1000 ppm cyanide, along with the background change from KOH to NaOH, facilitates standards makeup. A change from Tygon to Teflon tubing improved both the response time for fluids transit and simplified tubing replacement.

SECTION VI

FIELD EVALUATION

The cyanide monitor was installed in a field location to compare the monitor's performance with that of the laboratory method for total cyanides⁷ and to detect problems encountered in such an installation. There is a basic difference between these measurements so that it is expected that the monitor's results will be lower than those of the standard method. Orion requires that the sample pass a 1/32-inch-mesh strainer and the filter of the filter panel (Figure 4). Some cyanide metal complexes are not measured by the monitor. The standard method, however, involves direct sampling of the waste stream and the total cyanide is determined without interference. It was necessary for the monitor to be compared with an acceptable standard, and the only standard recognized by EPA is that of total cyanide.

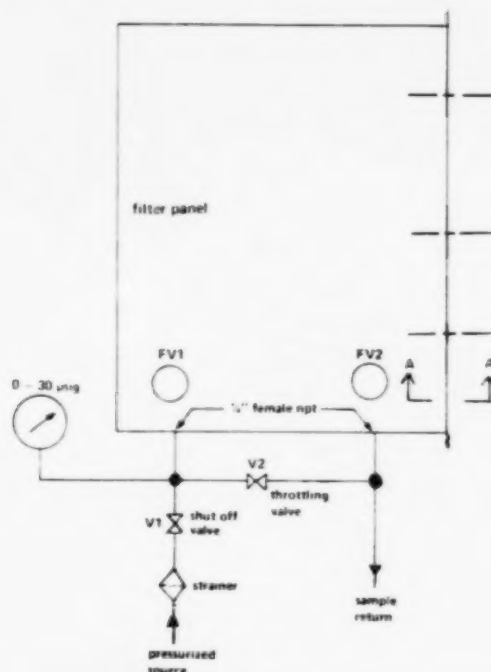


Figure 4. Fluid connections to monitor (courtesy of Orion Research Incorporated).

The standard cyanide procedure is quite lengthy, requires close attention, and involves the use of hazardous chemicals. Apparatus for five separate distillations were set up in the laboratory. A single analyst was able to make a maximum of eight sample determinations per day with this arrangement. The monitor, meanwhile, provides a continuous indication of the cyanide that it is capable of measuring. The monitor, then, can be useful to give estimates of the total cyanide, or it can be used as an indicator for the collection of samples when limits are exceeded. This is in addition to the industrial purposes for which it was designed.

A location to field test the cyanide monitor was found with the assistance of the Metal Finishers Foundation. W. T. O'Connell of Orion assisted with the installation of the monitor. Fluids connections consisted essentially of those shown in Figure 4. A Reliance, type CS, pump with garden hose connections was used to provide a sample input at the pressurized source shown. The plant effluent was discounted as a sampling source because of its high solids content. The sampling point selected was a sump located directly off the output of a rinsing process from cadmium and zinc plating baths. This point was not ideal for a continuous monitor because the sample flow was high during the one shift operating interval, but merely a shallow pool thereafter. The pool level was maintained overnight with a tap water supplement.

Problems were encountered with the fluids handling; some were not fully resolved. When sand and gravel clogged the inlet hose, which had merely been placed within the sump, the hose was inserted in a stainless-steel plating bucket within the sump and a strainer was attached on the hose inlet. The recommended 15 to 20 psi pressure input to the filter could not be maintained because of continual clogging of the throttling valve and strainer and the variations in flow between plant operating intervals and shutdown. The accommodations prevented pressures exceeding 25 psi, which could damage the filter, but as a result, the pressure ranged downward from settings made at 20 psi to as low as 5 psi.

An ISCO Model 1391 Water and Wastewater Sampler⁸ took 500 ml samples on a 3-hr cycle. The suction line strainer was also in the plating bucket along side the inlet hose. NaOH pellets were placed in each sample bottle to obtain pH greater than 11. Each morning these samples were removed and transported to the laboratory for chemical analysis.

At the time Orion installed and calibrated the cyanide monitor, a new electrode set was installed because of undesirable characteristics in electrode set B (of Table 3). When a wiring error in the CTA caused the power supply to the control circuit to fail, only the automatic restandardization feature of the measurement mode was lost. Thereafter, this feature was provided by manually calibrating each day. Also on a daily basis, the fluid connections were backflushed with tap water from the strainer. The strainer had been placed in series with the filter panel in an effort to reduce solids buildup on its screen.

A total of 33 samples were compared by the standard method for total cyanide with what was estimated to be equivalent values on the strip chart of the monitor. These comparisons were made assuming an 8-min transit time for the electrodes to respond to the same value as that of the sampler. The sampler required less than 1 min to fill the 500-ml bottle and purge the intake line. These data are illustrated in Table 4. The wide variation in the results of these comparisons are indicated in the column of percentage of monitor-versus-total-cyanide. The mean percentage was 64.2% with a standard deviation of 23.3%. It is not too surprising that the higher cyanide readings during plant operation reveal wide differences. Frequently, three separate cyclic excursions within a 1/2-hr interval were made in which changes as much as 40 mg/l cyanide occurred. The actual changes are probably greater because of the dampening affect of the long system-response time. The 1 to 5 mg/l overnight comparisons were still a disappointment, however, because the changes were minimal.

Table 4. COMPARISON OF CYANIDE MONITOR FIELD INSTALLATION
DATA WITH LABORATORY ANALYSIS OF TOTAL CYANIDE

Sample number	Cyanide monitor, mg/l	Cyanide total, mg/l	Difference mon.-total	$\%_T = \frac{\text{Monitor}}{\text{total}} \times 100$
15	48.0	51.7	-3.7	92.8
16	18.5	23.8	-5.3	77.7
17	5.6	6.4	-0.8	87.5
18	4.6	6.0	-1.4	76.7
19	4.8	5.3	-0.5	90.6
20	4.0	4.8	-0.8	83.3
21	36.0	60.2	-24.2	59.8
1A	1.3	10.6	-9.3	12.3
3A	1.5	2.1	-0.6	71.4
4A	1.6	2.6	-1.0	61.5
5A	1.4	2.5	-1.1	56.0
6A	1.3	2.3	-1.0	56.5
8A	35.0	65.4	-30.4	53.5
9A	23.0	42.2	-19.2	54.5
10A	15.0	41.2	-26.2	36.4
11A	16.0	25.1	-9.1	63.7
12A	1.6	3.7	-2.1	43.2
13A	1.2	2.5	-1.3	48.0
14A	1.3	3.0	-1.7	43.3
15A	1.2	3.2	-2.0	37.5
16A	20.0	44.6	-24.6	44.8
17A	45.0	64.1	-19.1	70.2
18A	40.0	31.2	+8.8	128.2
19A	14.8	22.0	-7.2	67.3
20A	1.35	2.5	-1.2	54.0
21A	0.76	1.9	-1.1	40.0
22A	1.6	2.7	-1.1	59.2
23A	1.15	2.3	-1.2	50.0
24A	9.2	8.6	+0.6	107.0
1B	28.0	40.5	-12.5	69.1
2B	17.0	16.5	+0.5	103.0
3B	2.4	4.1	-1.7	58.5
8B	7.0	11.3	-4.3	61.9

mean diff. = -6.2

mean % total = 64.2

The standard method for total cyanide requires significant laboratory bench space, and the continuous attention of an analyst because of the hazardous chemicals used. The expense of this usually prevents the routine analysis for total cyanide. The cyanide monitor may be useful for making routine estimates of the total cyanide when prior correlation studies indicate a consistent relationship with the standard method. For example, a regression analysis⁹ was performed with the data of Table 4. It is assumed that the expense and difficulty of obtaining total cyanide precludes its use for long periods. Therefore, the total cyanide, the difficult to obtain, is chosen as the dependent variable, or y-axis; and the monitor readings, the easily obtained, are made the independent variable, or x-axis. The derived regression line is determined from comparison readings over this short interval. Assuming good correlation, future readings of the monitor along with the regression line can be used to estimate the total cyanide. Figure 5 illustrates the estimate of the regression line for the results of this particular installation. The 95% confidence interval of the mean response is included. The standard deviation is 8.2826, with an estimated correlation coefficient of 0.921. Although better precision and accuracy would be desirable, the information obtained would be useful in studies of long-term trends.

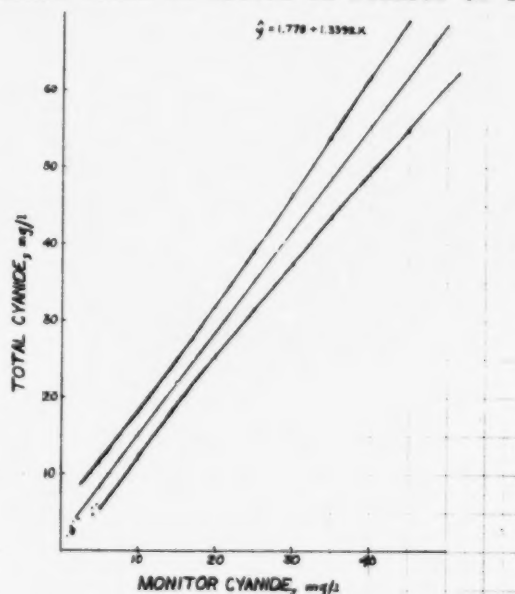


Figure 5. Regression line with 95% confidence limits for the mean response.

SECTION VII

LABORATORY TESTS WITH FIELD SAMPLE

The field installation of the cyanide monitor presented three types of problems: (1) the input sample pressure to the filter panel could not be continuously maintained, unattended, at the 15 to 20 psi recommended by Orion; (2) the rapidly changing cyanide concentrations were not represented accurately by the slowly responding fluid transit and electrodes; and (3) the cyanide of the sample was not accurately determined after straining and filtering.

The effect of the pressure variations on the system response was determined relatively. A tank with a fixed value of cyanide was operated with 20 psi pressure adjusted as input to the filter. The inlet hose was transferred to a 37.85-liter (10 gal) tank with a sample cyanide level 1 decade greater than the former. The inlet hose was returned to the original tank when the 37.85-liter tank emptied. The peak response indicated the relative response time. This was repeated for 10 psi and 5 psi pressure inputs to the filter panel. Table 5 displays the relative response times.

Table 5. RELATIVE SYSTEM RESPONSE WITH
VARYING PRESSURE INPUT

Inlet pressure, psi	Response time, minutes
20	9
10	12
5	14

Thus, the 5 minute difference in response between 20 psi and 5 psi could significantly change the monitor results during a rapidly increasing or decreasing comparison reading.

Six 18.93-liter (5 gal) samples of cyanide wastewater were obtained to make steady-state comparison between total cyanides as determined by the standard method and monitor readings. A sample was taken from within a tank source for the monitor and another was taken after transit through the strainers and filter. Total cyanides were determined with each of these samples and compared with monitor readings. Table 6 illustrates the results of these tests.

Table 6. LABORATORY TEST WITH CYANIDE WASTE SAMPLE
COLLECTED IN THE FIELD

Total cyanide, mg/l		Monitor response, mg/l	% Source	% Filtered
source	filtered			
7.1	5.7	5.3	74.6	93
11.5	9.9	10.0	87.0	101
14.8	13.4	13.0	88.0	97
17.7	14.9	16.0	90.0	107
16.7	13.4	12.0	72.0	90
20.6	15.9	15.0	73.0	94
Averages			80.8	97

The results show that the monitor's performance on steady-state samples is greatly improved over the performance exhibited in the field test. The pressure input was maintained at 20 psi. Stable equilibrium was attained after sample mixing before these comparisons were made. These data show that from 15% to 20% of the cyanide is removed by straining and filtering. Both the filtered total cyanide and the monitor have confirmed this when their results are compared with those of the total cyanide of the source. Also, for this particular plant's sample, essentially all of the cyanide metal complexes that pass the filter are converted to free cyanide and sensed by the monitor.

SECTION VIII

REFERENCES

1. Orion Newsletter, Vol. IV, Nos. 3 and 4, Orion Research Incorporated, Cambridge, Massachusetts, 1972.
2. Light, T. S., "Industrial Analysis and Control With Ion-Selective Electrodes," In: Ion-Selective Electrodes, Durst, R. A., (ed.), Washington, D.C., National Bureau of Standards Special Publication, 314, 1969.
3. Orion Newsletter, Vol. 1, No. 4, Orion Research Incorporated, Cambridge, Massachusetts, 1969.
4. Orion Newsletter, Vol 11, Nos. 5 and 6, Orion Research Incorporated, Cambridge, Massachusetts, 1970.
5. Orion Research Incorporated, Literature on Monitoring Systems - Series 1000 Monitors, Cambridge, Massachusetts.
6. Riseman, J. H., "Electrode Techniques for Measuring Cyanide in Wastewaters," American Laboratory, December 1972.
7. ASTM Standard, Part 23, Water; Atmospheric Analysis, p. 498, Method D2036-72 Referee Method A (1973).
8. Lauch, R. P., "Performance of the ISCO Model 1391 Water and Wastewater Sampler," unpublished report, U.S. Environmental Protection Agency, Office of Research and Development, NERC-Cincinnati, Cincinnati, Ohio, 45268, 1974.
9. Walpole, R. E., and Myers, R. H., "Probability and Statistics for Engineers and Scientists," The Macmillan Company, New York, 1972.